FLEXIBLE HOSE HAVING REDUCED FUEL VAPOR PERMEABILITY AND METHOD OF MANUFACTURING SUCH HOSE

Cross-Reference to Related Applications

This application is a continuation-in-part of Serial No. 09/071,634, filed February 7, 2002, which is a divisional of Serial No. 09/754,674, filed January 4, 2001, now U.S. Patent No. 6,365,250, which is a divisional of Serial No. 09/083,294, filed May 22, 1998, now U.S. Patent No. 6,203,873.

Background of the Invention

The present invention relates generally to hoses and particularly to fuel transport hoses such as fuel filler and fuel filler neck hoses having reduced permeability to fuel vapors. More particularly, this invention relates to fuel hoses constructed from fluoropolymers.

Recent environmental regulations imposed on the automotive industry severely limit the amount of fuel vapor that can permeate from the fuel systems of motor vehicles. Choosing the right polymer to provide high performance, long service life, and reduced permeability of fuel in the fuel systems of automotive vehicles while maintaining costs at an acceptable level has been more difficult for automotive designers than ever before. A particular permeation problem associated with prior art fuel hoses involves the high permeation of fuel vapor along the surface of one of the barrier layers. Typically, fuel transfer and fuel vapor hoses include a butadiene-acrylonitrile rubber inner tubular member and a fluoroplastic barrier layer around the nitrile inner tubular layer as described in U.S. Patent No. 5,639,528 to Feit et al.; however, such hoses have a high permeability to fuel, high fuel extraction, poor ozone resistance, poor heat aging and poor sour gas resistance. Other hoses have included a fluoroelastomer as the inner wall surface of the hose, but such hoses have a higher permeability to fuel vapors.

Other attempts to produce a fuel filler neck hose with reduced permeability to fuel vapors used a tetrafluoroethylene-hexafluoropropylene-vinylidene fluoride terpolymer liner and a thicker layer of hexafluoropropylene-vinylidene fluoride copolymer or other suitable material as the conductive inner tubular structure. See, for example, U.S. Patent Nos. 4,606,952 to Sugimoto and 5,430,603 to Albino et al. Such hose structures have a tendency to wrinkle on the inner radius of the forming mandrel or pin causing a cosmetic defect.

Accordingly, there is a need for an improved fuel hose that meets present industry standards and is still relatively cost efficient.

Summary of the Invention

It is an object of the present invention to provide a hose, which is particularly useful as a fuel transport hose wherein the hose not only has improved fuel vapor barrier properties but also is reasonably economical to manufacture. In accordance with the invention, the hose comprises a plurality of layers comprising a first fluoropolymer barrier layer forming a first tubular structure, and an elastomeric layer forming a second tubular structure around the first fluoropolymer, and a cover layer providing an outer surface of the hose. The hose of the present invention may further comprise one or more additional layers such as a reinforcing layer between the elastomeric layer and the cover layer.

It is another object of the present invention to provide a method for the manufacture of such hose.

In one embodiment of the present invention, the hose comprises a first tubular structure comprising a blend of a first fluoropolymer and a second fluoropolymer wherein the first fluoropolymer exhibits elastomeric characteristics and the second fluoropolymer exhibits thermoplastic characteristics; a second tubular structure which comprises an elastomeric material such as butadiene-nitrile rubber, epichlorohydrin, ethylene-acrylate rubber, and the like.

In addition to the barrier layers, the hose of the present invention may also include one or more elastomeric tubular layers and/or a reinforcing layer between the outermost tubular structure and the protective cover layer.

The hose of the present invention not only reduces the permeation of hydrocarbon vapors through the various layers, but also prevents the flow of fuel vapor along the various layers where it can be released to the atmosphere through the ends of the hose. In addition, the present hose is superior to prior art hoses which employ a nitrile rubber inner layer and a fluoropolymer over the nitrile layer. The present hose not only has good low temperature properties, has good push-on values, exhibits extended service life, and can be produced as a smooth, uniform tubular structure without wrinkles caused by sharp turns, curves and bends during the formation of the hose on a forming mandrel or pin, but it also has other superior properties such as improved fuel extraction properties, improved ozone resistance, improved heat aging properties, and improved sour gas resistance.

Brief Description of the Drawings

FIG. 1 is a perspective cutaway view of a tubular member which illustrates one manifestation of a first embodiment of the invention; and

FIG. 2 is a perspective cutaway view of a tubular member that illustrates another manifestation of the first embodiment of the invention.

Detailed Description of the Invention

In accordance with one aspect of the invention, a flexible fuel hose having improved fuel vapor barrier properties comprises: a blend of fluoropolymers as a barrier layer forming an inner tubular structure, and an elastomeric layer forming a second tubular structure around the inner tubular structure, and a protective outer cover layer. The fluoropolymer barrier layer comprises a blend of about 5 to 95 weight percent of a first fluorointerpolymer having a fluorine content of about 68 to 74%, and about 95 to 5 weight percent of a second fluoropolymer having a fluorine content of about 73 to 78%. The first fluoropolymer comprises a copolymer or terpolymer formed of two or more monomers selected from the group consisting of hexafluoropropylene, vinylidene fluoride and tetrafluoroethylene, and the second fluoropolymer comprises a terpolymer formed by the copolymerization of hexafluoropropylene, vinylidene fluoride and tetrafluoroethylene, wherein the first fluoropolymer exhibits elastomeric characteristics and the second fluoropolymer exhibits thermoplastic characteristics. The second tubular structure is an elastomeric layer; and a protective cover is an elastomer material.

In another aspect of the invention, a method for manufacturing the flexible fuel hose of the invention comprises: providing a first conductive barrier layer comprising a blend of about 5 to 95 weight percent of a first fluoropolymer having a fluorine content of about 68 to 74%, with about 95 to 5 weight percent of a second fluoropolymer having a fluorine content of about 73 to 78%, said first fluoropolymer comprising a copolymer or terpolymer formed of two or more monomers selected from the group consisting of hexafluoropropylene, vinylidene fluoride and tetrafluoroethylene, and the second fluoropolymer comprising a terpolymer formed by the copolymerization of hexafluoropropylene, tetrafluoroethylene, and vinylidene fluoride monomers, wherein the first fluoropolymer exhibits elastomeric characteristics and the second fluoropolymer exhibits thermoplastic characteristics; providing a second elastomeric layer comprising a butadiene-nitrile rubber, epichlorohydrin, ethylene-acrylate rubber, etc., providing a cover layer comprising butadiene-rubber, epichlorohydrin, ethylene-acrylate rubber, and the like; extruding the first conductive fluoropolymer barrier layer to form a first tubular structure; extruding the elastomeric layer in a telescoping relation on said first extruded fluorointerpolymer tubular structure forming an elastomer extruded tubular structure thereon; and applying a protective cover surrounding the second extruded elastomeric tubular structure.

Referring to the Drawings, FIGS. 1-2 illustrate a hose of the present invention wherein the first barrier layer of the hose comprises a blend of a fluoroelastomer with a fluoroplastic and the second layer is an elastomeric material. More specifically, FIG. 1 illustrates a hose 100 comprising a first fluoropolymer barrier layer 10 forming the interior wall of the hose 100, a second elastomeric layer 12 adjacent to and surrounding the first fluoropolymer barrier layer 10, and a cover layer 16 adjacent to and surrounding the second elastomeric layer 12.

FIG. 2 illustrates another hose 200 comprising a first fluoropolymer barrier layer 10 forming the interior wall of the hose 200, a second elastomeric layer 12 adjacent to and surrounding the first barrier layer 10, a reinforcing layer 14, and a cover layer 16 adjacent to and surrounding the reinforcing layer 14.

The term "fluoropolymer" as used herein refers to polymers produced from two or more fluoromonomers and, is meant to encompass fluoropolymer blends, copolymers and terpolymers, of fluoropolymers, and blends thereof.

The term "hydrocarbon" as used herein is meant to include fuels such as gasoline, oils, air conditioning gases, organic chemicals, and the like.

The first barrier layer 10 of the invention is a blend of two or more fluoropolymers wherein at least one of the fluoropolymers is characterized as having elastomeric characteristics and at least one of the fluoropolymers is characterized as having fluoroplastic characteristics. Preferably, the first barrier layer 10 is a blend of a fluoroelastomeric hexafluoropropylene-vinylidene fluoride copolymer or a fluoroelastomeric vinylidene fluoride-hexafluoropropylene-tetrafluoroethylene terpolymer, blended with a fluorothermoplastic tetrafluoroethylene-hexafluoropropylene-vinylidene fluoride terpolymer. Most preferably, the fluoroelastomer component on the blend has a fluorine content of about 65 to 75% and the fluoroplastic component of the blend has a fluorine content of about 73 to 78%. The hexafluoropropylene-vinylidene fluoride fluoroelastomer is commercially available from DuPont under the name Viton A, Viton E445 or Viton 60. The vinylidene fluoride-hexafluoropropylene-tetrafluoroethylene fluoroelastomer is commercially available from 3M under the name Fluorel FT2350 or FE58300QD. The tetrafluoroethylene-hexafluoropropylene-vinylidene fluoride fluoroplastic terpolymer is commercially available as Dyneon THV from Dyneon.

The blend which forms the first fluoropolymer barrier tubular structure comprises about 5 to 95 weight percent fluoroelastomer component and about 95 to 5 weight percent fluoroplastic component. Typically, the first fluorointerpolymer may contain about 5 to 50 weight percent fluoroelastomeric component and about 95 to 50 weight percent fluorothermoplastic component and, most typically, about 5 to 70 weight percent fluoroelastomer component and about 95 to 30 weight percent fluorothermoplastic component. Since the permeability of the fuel hose to fuel

vapors decreases with an increase in the fluorine content of the blend, a higher ratio of the fluoroplastic component which typically contains a higher percentage of fluorine by weight than the fluoroelastomer component may be employed in the blend 10; however, the plastic-like properties of the fluorothermoplastic components are prone to cause kinking of the hose when the fluorothermoplastic component is too high. Typically, the fluorine content of the fluoroelastomer component of the blend is about 68 to 74% and the fluorine content of the fluorothermoplastic component of the blend is about 73 to 78%. Such blends have been found to provide a good balance between reduced fuel vapor permeability and good physical properties of the hose. Typically, the thickness of the barrier layer 10 is about 5 to 25 mils, preferably about 13 to 14 mils.

The second layer 12 of the hose of the present invention is an elastomeric material such as acrylonitrile-butadiene rubber, epichlorohydrin, ethylene-acrylate, and the like.

The compositions of the present invention are either unvulcanized or vulcanized using any of the art established vulcanizing agents such as peroxides, polyols, polyamines, etc. The peroxide vulcanizing agent includes, for example, dicumyl peroxide, 2-5-dimethyl-2, 5-di(t-butylperoxy) hexyne-3, etc. The polyol vulcanizing agent includes, e.g., hexafluoroisopropylidene-bis (4-hydroxyphenyl-hydroquinone, isopropylidene-bis(4-hydroxyphenyl), and the like. The polyamine vulcanizing agent includes, e.g., hexamethylenediamine carbamate, alicyclic diamine carbamate, etc. The amount of vulcanizing agent employed is generally that which is customarily used in the art. Typically, about 0.5 to 10% vulcanizing agent is employed depending upon the vulcanizing agent employed.

The elastomer layer 12 may be a synthetic elastomer such as an acrylonitrile-butadiene rubber, ethylene-acrylate rubber, and the like.

The outer cover 16 of the hose is a protective layer of any commercially recognized materials for such use such as elastomers, thermoplastic polymers, thermosetting polymers, and the like. Typically, the protective layer is a synthetic elastomer having good heat resistance, oil resistance, weather resistance and flame resistance. Preferably, the outer cover layer is a synthetic elastomer selected from the group consisting of styrene-butadiene rubber (SBR); butadiene-nitrile rubber such as butadiene-acrylonitrile rubber; chlorinated polyethylene; chlorosulfonated polyethylene; vinylethylene-acrylic rubber, acrylic rubber, epichlorohydrin rubber such as Hydrin 200, a copolymer of epichlorohydrin and ethylene oxide available from DuPont ECO; polychloroprene rubber (CR); polyvinyl chloride; ethylene-propylene copolymers (EPM); ethylene-propylene-diene terpolymer (EPDM); ultra high molecular weight polyethylene (UHMWPE); high density polyethylene (HDPE); and blends thereof. Preferably, the synthetic elastomer is chloroprene.

The reinforcing member 14 is a material that affords physical strength to the finished hose. Typically, the reinforcing member is a natural or synthetic fiber selected from the group consisting of glass fibers, cotton fibers, polyamide fibers, polyester fibers and rayon fibers. In some instances the reinforcing member may be metal wire. Preferably, the reinforcing material is an aromatic polyamide such as Kevlar or Nomex both of which are manufactured by DuPont. The reinforcing material may be knitted, braided or spiraled to form the reinforcing member. In a preferred aspect of the invention, the reinforcing material is spiraled around a tubular structure. While the reinforcing layer may be a preferred component of the hose structure, it is not critical and may or may not be employed in the manufacture of certain hoses depending upon the requirements of the manufacturer.

As is common practice in the industry, the innermost layer of the hose of the present invention, the barrier layer 10, is made conductive to prevent the build-up of static electricity generated by the flow of fuel along the inner surface of the hose. Typically, the inner barrier layer 10 is made conductive by compounding the layer material with carbon black or other industry recognized ingredients to provide conductivity to the barrier layer. While the amount of conductive material added is not critical, excess conductive material such as carbon black tends to make the material more difficult to process. In vapor or vent applications, the innermost layer of the hose need not be conductive.

In the invention, as shown in Figs. 1-2, the first barrier layer 10 forms the inner tubular wall structure of the fuel transfer hose and, typically, is a conductive blend of a fluoroelastomer and a fluorothermoplastic wherein the fluorine content of the fluoroelastomer is about 68 to 74% and the fluorothermoplastic is about 73 to 78%. Preferably, the blend 10 is made conductive by incorporating carbon black into the composition, in a sufficient amount to prevent a build-up of static electricity.

Methods of producing fuel transfer hoses are known in the art. For example, separate extrusion, tandem extrusion or coextrusion processes may be used. For versatility and cost reasons, the preferred methods for producing the fuel filler transfer hoses of the present invention are separate extrusion and tandem extrusion.

In a preferred embodiment, the manufacture of the fuel hose of the present invention is as follows: The conductive first fluoropolymer barrier layer comprising a blend of about 5 to 95 weight of a first fluoropolymer comprising a copolymer, terpolymer or a mixture thereof formed from two or more monomers selected from the group consisting of hexafluoropropylene, vinylidene fluoride and tetrafluoroethylene, with about 95 to 5 weight percent of a second fluoropolymer, said second fluoropolymer comprising a copolymer, terpolymer or mixture thereof formed by the

copolymerization of two or more monomers selected from the group consisting of hexafluoropropylene, vinylidene fluoride and tetrafluoroethylene, is extruded into a tube and then immediately fed through another extruder during which the second barrier layer comprising a fluorothermoplastic of hexafluoropropylene-tetrafluoroethylene-vinylidene fluoride is applied. After the tube has been extruded and the appropriate layers, including any elastomeric layer, is applied, strands of reinforcing fibers such as Kevlar are applied, preferably by spiraling, to the tubular structure. A protective cover such as chloropolyethylene is then applied onto the reinforced tube, preferably, by a cross-head extruder. The chloropolyethylene is drawn down onto the reinforced tubular structure by use of a vacuum. The covered reinforced tube is then placed on a mandrel and vulcanized. The formed hose is then manually removed from the mandrel.

Other polymers, e.g., fluorinated ethylene-propylene (FEP) copolymers such as Teflon, which is available from DuPont, may be used as a component in the preparation of the blend of the first barrier layer.

Other additives such as antioxidants, processing aids, etc. can be employed in carrying out the present invention and it is within the scope of this invention to incorporate herein any such additives as commonly used in making fuel line hoses.

The blended fluoroelastomer/fluorothermoplastic barrier layer of the present invention is useful in reducing the permeability of fuel vapor from the fuel transfer hose; however, it is also useful in reducing the permeability of chemical vapor such as those used in air conditioning hoses, oil hoses, and the like where severe chemical resistance or vapor permeation resistance is required.

The use of the first fluoropolymer barrier layer and the second elastomeric layer, in accordance with the present invention, to manufacture fuel filler neck hoses and fuel transfer hoses, unexpectedly achieves almost complete impermeability of fuel vapors from the hose.

EXAMPLE

In order to demonstrate the advantages of a fuel hose of the present invention, several hoses (A) prepared in accordance with the present invention were provided. Each of the hoses had an inner layer consisting of a blend containing about 95 weight percent of a first fluoroelastomer having a fluorine content of about 68 to 74%, and about 5 weight percent of a second fluorothermoplastic having a fluorine content of about 73 to 78%. A similar number of other hoses (B) representative of prior art hoses had a nitrile (NBR) inner layer and a tetrafluoroethylene-hexafluoropropylene-vinylidene fluoride terpolymer (THV) layer surrounding the inner NBR layer.

All of the hoses were subject to identical treatments that included fuel extraction, ozone resistance, tensile, elongation, and heat aging. The results are shown in TABLE 1.

TABLE 1

Sample	A	B
Fuel extraction, grams/square meter[1]	1.3 - 1.9	42.5 -77
Ozone Resistance[2]	No Cracks and Tears	Many Cracks and Tears
Tensile	-14%	-53%
Elongation	-4%	-53%
Heat Aging[3]	Bent with no signs of cracks	Very brittle and cracked when bent

1 - Measured by filling the hose with fuel and holding for 24 hours; pouring off the fuel; evaporating the fuel and measuring the extracted material.
2 - Subjecting inner layer of hose to one hundred parts per hundred million of ozone.
3 - Aging slabs of inner tube of hose for 7 days @150° C running bend tests

While the use of a first barrier layer comprising a fluoroelastomer/fluorothermoplastic blend comprising a hexafluoropropylene-tetrafluoroethylene-vinylidene fluoride terpolymer are particularly useful in hose construction to reduce permeability of fuel vapor, the combination of such first fluorointerpolymer barrier layer comprising a fluoroelastomer/fluorothermoplastic blend and an elastomer layer comprising acrylonitrile-butadiene rubber, epichlorohydrin, ethylene-acrylate rubber, and the like can be used in the manufacture of other articles where reduced fuel or hydrocarbon vapor is desired, such as in the manufacture of O-rings, gaskets, diaphragms, etc.

Having illustrated and described the present invention in detail and by reference to preferred embodiments thereof, it will be apparent that modifications and variations are possible without departing from the scope of the invention defined in the appended claims.

What is claimed is: